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The Cation Radical of Tetramethyl-2-tetrazene

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Abstract: The reaction between tetramethyl-2-tetrazene and tetranitromethane in various solvents gives a relatively long-lived paramagnetic species which has been identified by its electron paramagnetic resonance spectrum as the cation radical of tetramethyl-2-tetrazene. Although the complexity of the spectrum precluded analysis by inspection, spin-coupling constants were determined by least-squares analysis of a portion of the spectrum. These parameters agreed with values obtained for similar radicals. The coupling constants (in gauss) for the radical in acetone are a_N (2,3 positions) = 1.07 ± 0.05 , a_N (1,4 positions) = 10.93 ± 0.05 , a_H (six equivalent protons) = 10.45 ± 0.05 , and a_H (six equivalent protons) = 11.72 ± 0.05 ; the line width is 0.39 gauss at -30° . The free electron spin density is estimated to be 0.42 on the 1,4 positions and 0.08 on the 2,3 positions. The relatively small nitrogen coupling constant in the 1,4 positions compared to that predicted for tetrahedral nitrogen atoms is evidence for sp^2 hybridization on the terminal nitrogen atoms. It is found that reactions of tetranitromethane with other materials result in paramagnetic positive ions of the oxidized species.

During an investigation of the chemistry of 1,1,4,4-tetramethyl-2-tetrazene, $(CH_3)_2NN=NN(CH_3)_2$ (TMT), it was found that this compound reacted with tetranitromethane (TNM) in chloroform to give a reddish brown solution. The nuclear magnetic resonance spectrum of the solution at -40° had broad lines, which sharpened as the color faded. The presence of a paramagnetic material causing the rapid nuclear spin relaxation was confirmed by observation of an esr spectrum.

TMT is a good electron donor, as observed in the complexes formed with $Al(CH_3)_3$ ^{2a} and other electron acceptors.^{2b} Free radicals have been observed as intermediates during the pyrolysis of this material.³ It has been shown that reactions involving TNM may result in free radicals.⁴⁻⁶ Buck, *et al.*,⁴ find that the reaction of TNM with some aromatic compounds gives a solid with a broad resonance and unresolved hyperfine splitting; the spectrum was attributed to a charge-transfer complex. Lagercrantz⁵ finds that irradiating certain unsaturated organic compounds in TNM with visible light results in an apparent transfer of one or two nitro groups from TNM to the unsaturated compound inside an electron-donor-acceptor complex. Further studies⁶ have found free radicals in reaction mixtures of TNM with unsaturated compounds in alkaline media. The present study indicates that in some cases TNM may be used effectively as an electron acceptor, the observed free radical being the positive ion of the electron donor.

Experimental Section

TMT was prepared by the oxidation of 1,1-dimethylhydrazine with mercuric oxide, following methods previously employed.⁷

(1) (a) U. S. Naval Postgraduate School; (b) U. S. Naval Ordnance Test Station.

(2) (a) N. R. Fetter, F. E. Brinckman, and D. W. Moore, *Can. J. Chem.*, **40**, 2184 (1962); (b) W. E. Bull, J. A. Seaton, and L. F. Audrieth, *J. Am. Chem. Soc.*, **80**, 2516 (1958).

(3) B. G. Gowenlock, P. P. Jones and D. R. Snelling, *Can. J. Chem.*, **41**, 1911 (1963).

(4) H. M. Buck, J. H. Lupinski, and L. J. Oosterhoff, *Mol. Phys.*, **1**, 196 (1958).

(5) C. Lagercrantz and M. Yhland, *Acta Chem. Scand.*, **16**, 1807 (1962).

(6) C. Lagercrantz, *ibid.*, **18**, 382 (1964).

(7) W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.*, **79**, 572 (1957).

Samples of TNM-TMT solutions were obtained by distilling under vacuum both reactants separately along with about 1 ml of solvent into a specially constructed receiver at liquid nitrogen temperatures. The reaction mixture was then warmed to about -40° , agitated, and transferred by tilting into a 1-mm side arm attached to the receiver. The capillary tube was then sealed, removed, and stored at liquid nitrogen temperature until examination. Since the lifetime of the radical at room temperature was only a few minutes, esr observations were made on the sample cooled with a flow of nitrogen gas. Electrolytic production of radicals *in situ* was accomplished by passing current between two platinum gauze electrodes in an evacuated Varian flat cell. Voltage and current were varied over a wide range, resulting in a change of the spectrum intensity only. Chemical production of radicals was studied by flowing solutions of the two reactants into a cell similar to the one described by Dixon and Norman.⁸ The solutions were deoxygenated by bubbling nitrogen through them for 10 min, then introduced into two syringes held in an infusion pump. Flow rates of from 0.2 to 30 cc/min were obtainable, resulting in a minimum time between mixing and taking spectra of about 1 sec. The esr spectra were taken on a Varian V-4500 spectrometer with a 9-in magnet, using 100-kc modulation.

Assignment of Spectral Parameters

The observed spectra were temperature dependent and also changed slightly with solvent. Overlap of the large number of lines was considerable, and a search was made for a solvent and a temperature which would give as detailed a picture of the hyperfine structure as possible. Chloroform, acetonitrile, tetrahydrofuran, dimethoxyethane, and acetone were tried as solvents, spectra being observed in each case.

The spectrum of the radical produced by direct reaction between TNM and TMT in acetone at -30° with reactant concentrations each 0.0005 *M* is shown in Figure 1. The sample was placed in a sealed capillary. These conditions give spectra having optimum resolution of the hyperfine structure. Only the central portion of the spectrum is displayed; lines further away from the center are weaker and are obscured by instrument noise.

The determination of the coupling constants was not a trivial problem for this complex spectrum. The procedure is complicated by the fact that the basic multiplet intensity of two nitrogen atoms (1:2:3:2:1) and of six hydrogen atoms (1:6:15:20:15:6:1) each

(8) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

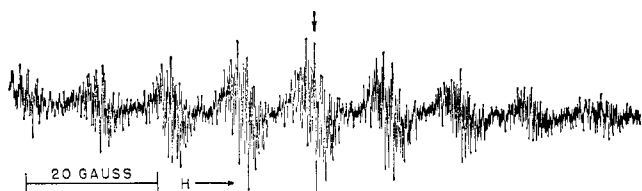


Figure 1. The central portion of the esr spectrum of the cation radical of tetramethyl-2-tetrazene in acetone at -30° . The intensity of the signal decreased slightly during the 100-min sweep. The spectrum reproducibly exhibits a slight asymmetry about its center (indicated by arrow above).

have five strong lines in approximately the same intensity ratio.

Attempts in fitting the spectrum assuming twelve equivalent hydrogen atoms resulted in very poor agreement, indicating all four methyl groups are not equivalent. An initial assignment of coupling constants was made by trial and error assuming four sets of multiplets each with an intensity ratio of 1:2:3:2:1. The distance from the center of the spectrum to one of the nearest strong lines was taken as a trial coupling constant for each set of equivalent nuclei. The various possible permutations of the four coupling constants were systematically investigated, resulting in only one combination which clearly showed agreement with the experimental spectrum. The coupling constants are given in Table I. One coupling constant is small; three are large and nearly equal. A comparison of the coupling constants for other radicals having N-methyl groups is useful. Wurster's blue cation,⁹ the positive ion of tetrakis(dimethylamino)ethylene,¹⁰ the trimethylamine cation,¹¹ and the positive ion of N,N'-tetramethylbenzidine,¹² each show the nitrogen coupling constant to be within a factor of 2 of the coupling constant of the methyl hydrogens, and in most cases the two coupling constants are nearly equal. Hydrogen and nitrogen coupling constants on amino groups follow a similar pattern.¹³ This suggests that in the TMT case the small coupling constant belongs to the 2,3-nitrogen atoms; the three large coupling constants belong to the two inequivalent sets of six hydrogens each and the set of 1,4-nitrogens. The critical problem in the analysis of this spectrum is to deduce the proper assignments of these three parameters.

Table I. The Coupling Constants of Tetramethyl-2-tetrazene Cation Radical in Acetone at -30°

a_N (2,3-N atoms) = 1.07 ± 0.05 gauss
a_N (1,4-N atoms) = 10.93 ± 0.05 gauss
a_H (six protons) = 10.45 ± 0.05 gauss
a_H (six protons) = 11.72 ± 0.05 gauss
$g = 2.0034 \pm 0.0001$

Because of the many overlapping lines (1225 lines predicted), a change in any one of the coupling constants by as little as 0.01 gauss produces a noticeable change in the shape of the spectrum envelope. The refined adjustment of each of the four coupling constants by

(9) J. R. Bolton, A. Carrington, and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 615 (1962).

(10) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964).

(11) A. J. Tench, *J. Chem. Phys.*, **38**, 593 (1963).

(12) J. M. Fritsch and R. N. Adams, *ibid.*, **43**, 1887 (1965).

(13) M. T. Melchior and A. H. Maki, *ibid.*, **34**, 471 (1961).

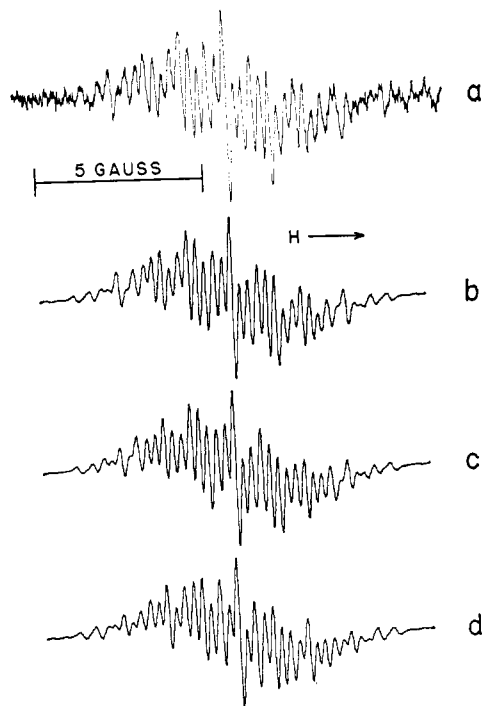


Figure 2. The central grouping of lines of the esr spectrum of tetramethyl-2-tetrazene cation radical in acetone at -30° : (a) experimental; (b) computer-simulated spectrum of least-squares fit assuming $a_N = 10.93$ gauss; (c) same as b with alternate assumption that $a_N = 10.45$ gauss; (d) same as b with alternate assumption that $a_N = 11.74$ gauss.

trial and error was a tedious procedure. A digital computer program was therefore written to refine these parameters using the method of least squares. (The central grouping of lines was converted to 181 digital points by reading the coordinates from graph paper.) The program calculated the spectrum envelope by computing the value of the derivative of the Lorentzian line shape function at each of these points. The derivative matrix was then evaluated numerically by varying the four coupling constants, the envelope height, the line width, and the positioning of the center of the spectrum. Positioning of the lines along the field direction was quite important because of the steep slopes involved.

Three iterations were generally sufficient to obtain convergence and the best values of the parameters. In some cases divergence was noticed for a poor starting approximation. Fifteen minutes of CDC-1604 computing time was required for the three iterations on these 181 points. The results of the least-squares fit were most gratifying and are shown on lines b, c, and d of Figure 2 for the assignment of the 1,4-nitrogen atoms to the coupling constant of (b) 10.93 gauss, (c) 10.45 gauss, and (d) 11.74 gauss, all with a line width of 0.39 gauss. The sum of the squares of the errors (on a relative basis) for each of these plots is (b) 21.6, (c) 35.9, and (d) 37.0. The superior fit for computed spectrum b indicates that this is the proper assignment. The coupling constants determined in this manner are presented in Table I; g was determined by simultaneously taking a spectrum of the radical and of the peroxyamine disulfonate ion ($g = 2.0055$) at room temperature.

The asymmetry of the spectrum in Figure 1 is reproducible and is not due to instrumental shortcomings.

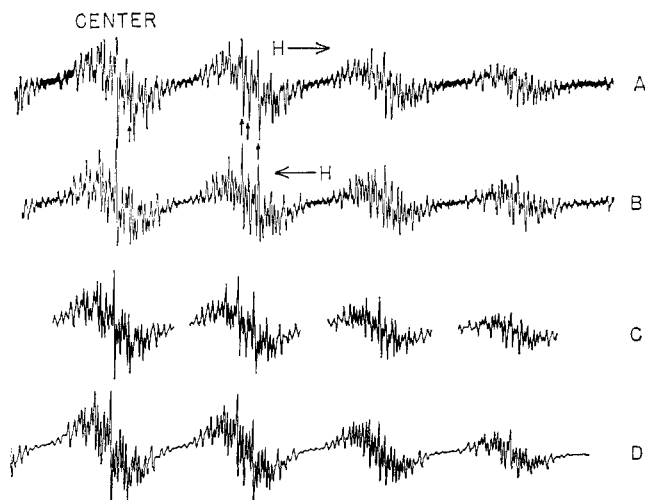


Figure 3. The esr spectrum of the tetramethyl-2-tetrazene cation at -15° in acetone. Concentration is $0.001 M$: (a) The high-field side of spectrum; (b) the low-field side of spectrum, with the ordinate and abscissa polarity reversed for comparison with the high-field spectrum; (c) the average of lines a and b; (d) computer-simulated esr spectrum with parameters presented in text. The distances from the center to the vertical arrows indicate the observed coupling constants.

The asymmetry is again illustrated in Figure 3, where the spectrum of a solution with each reactant equal to $0.001 M$ concentration at -15° is displayed. The increased concentration as compared to the conditions in Figure 1 results in slightly broader lines, but an improved signal-to-noise ratio. Line A is the spectrum of the center and the three groupings of lines to the high-field side. Line B is the center and the three groupings of lines to the low-field side, taken experimentally by reversing the polarity of the leads to the ordinate and the abscissa of an X - Y recorder to maintain the same phase as in line A. The field was swept from left to right in each case. In the absence of asymmetry lines A and B should appear identical.

The usual first approximation made in the prediction of esr spectra in solution is to calculate the line positions to first order and to assume the line widths are constant for all transitions. Second-order shifts are observed with nuclei having a spin of unity or greater, such as is the case with the interaction of an electron with a nitrogen nucleus. The inclusion of these second-order effects introduces slight but noticeable shifts from the positions of the lines predicted to first order. The most noticeable effect is to shift lines asymmetrically, such that as transitions on one side of the center are shifted further away from the center, lines on the other side are shifted toward the center.

This being the case, an averaging of the spectrum on one side of the center with the spectrum on the other side of the center will tend to cancel second-order contributions to asymmetry. Line C in Figure 3 is constructed from lines A and B for this purpose. The value of each maximum and minimum in line A was averaged with the corresponding maximum or minimum in line B, and straight lines were drawn between neighboring maxima and minima averages to obtain line C. The computer simulated spectrum is displayed in line D. The agreement between lines C and D is unmistakable, and considerably better than that obtained

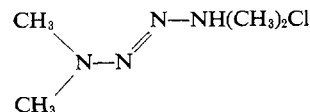
with the other possible assignments considered in Figure 2.

A verification of the fact that the paramagnetic species is the positive ion of TMT was made by oxidizing TMT electrolytically in the absence of tetranitromethane. Current was passed between two platinum electrodes, with the positive electrode in the sensing region of the cavity. Tetrapropylammonium perchlorate ($0.1 M$) was used as the supporting electrolyte, and acetone was again used as the solvent. A spectrum was obtained which closely resembled that taken at lower temperatures. To be certain that the TNM was not causing measurable changes in the coupling constants, the room temperature spectrum was obtained of the radical produced by reaction with TNM in a flow system. Because of line width and coupling constant variations, only half as many lines appear to be resolved at room temperature as at -30° . The spectra of the radical produced electrolytically and that produced chemically are identical at room temperature.

It is interesting to note that TNM is a good oxidizing agent for other easily oxidized materials. Using the flow system, TNM and *p*-phenylenediamine were treated in $0.001 M$ concentrations producing a strong esr signal of the positive ion of *p*-phenylenediamine, as determined by comparison with previous work.¹³ *o* and *m*-Phenylenediamine with TNM did not give paramagnetic species. No other radicals were detected in the reaction mixtures.

Discussion

The information obtained from the esr analysis may be used to support some conclusions concerning the structure of the radical. The appearance of two inequivalent sets of equivalent pairs of methyl groups means there is rotational hindrance about the N-N single bond. The observed line width of 0.39 gauss is not limited by instrumental shortcomings since line widths of 0.05 gauss have been observed with the same system. The lifetime of a given configuration is thus greater than 10^{-6} sec with respect to interchange of the methyl groups. In a related study of the protonation of TMT in nonaqueous media, the authors have observed the effect of rotational hindrance. The 60-Mc nmr spectrum of the tetrazenium hydrochloride, below, in $CDCl_3$ at -30° shows the structure to be



The 1-substituted methyl groups are split 24 cps by structural nonequivalence. Heating the solution causes the methyl lines to broaden and coalesce as the rate of exchange becomes equal to, then exceeds the critical 24-sec^{-1} rate. The nmr spectrum of TMT in the same solvent shows no evidence of rotational hindrance at temperatures as low as -70° .

The free electron is very likely in a nitrogen p orbital in the 1,4 positions, since the nitrogen coupling constant (10.93 gauss) is relatively small compared to the 80 gauss^{11,14} expected for sp^3 hybridization of these nitrogen atoms.

(14) T. Cole, H. Pritchard, N. Davidson, and H. McConnell, *Mol. Phys.*, **1**, 406 (1958).

The nitrogen coupling constants are not proportional to the spin density on the nitrogen atom alone, but depend to some degree upon neighboring spin densities.^{15,16} An approximate unpaired electron spin density may be obtained for comparison with calculations by assuming that the hydrogen coupling constant is proportional to the spin density on the nitrogen to which the methyl group is attached.¹⁷ $(\text{CH}_3)_3\text{N}^+$ is considered as a reference,¹¹ for which the isotropic hydrogen coupling constant is 26.7 gauss. A coupling constant of 10.45 gauss for one set of hydrogen atoms and of 11.74 gauss for the other would then give an approximate unpaired electron density on the 1 and 4 positions of 0.42. The spin density on the 2 and 3 positions would then be 0.08.

It is interesting to compare the spin distribution determined above with that of the butadiene anion radical.¹⁸ The two systems have the same number of π electrons in approximately the same geometrical configuration. Calculations of the spin density were made using the Hückel molecular orbital method. There are no generally accepted values for the Coulomb integrals, α , and the resonance integrals, β , for TMT^+ . In general there will be two Coulomb integrals: α_1 for the atoms in the 1 and 4 positions, and α_2 for those in the 2 and 3 positions. Resonance integrals will be represented by β_{ij} for the integral between atoms i and j .

A model was chosen in which

$$\alpha_1 = \alpha_2 + h\beta_{2,3}$$

and

$$\beta_{1,2} = \beta_{3,4} = k\beta_{2,3}$$

where h and k are unknown. The electron distribution is uniquely determined for given values of h and k using the simple Hückel approach. The overlap integral was neglected in the calculations; the information obtained by including it results in a similar picture with slightly different values of the parameters.

It is a matter of simple matrix algebra to show that, for the above model, when there are five electrons in the π system, the ratio r of the spin density in position 1 to that in position 2 is related to the other parameters by the equation

$$k = \frac{\sqrt{r}}{r-1}(1-h) \text{ for } r > 1 \text{ and } h < 1$$

For the butadiene anion, h is generally accepted to be equal to zero; r is observed to be 2.73, giving a value of k equal to 0.955. This is close to 1 and is what would be expected for equal bond lengths and a planar π -orbital system.

For TMT^+ , h is probably in the range of from 0.5 to 1; r is 5.25. This gives an estimated value for k of 0.15 ± 0.15 . The small value of k for TMT^+ indicates little interaction between positions 1 and 2 (3 and 4 also) and indicates that the orbitals may not form a planar π system, but rather show a significant twist away from planarity in the 1,2 and 3,4 positions.

(15) M. Karplus and G. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(16) E. W. Stone and A. H. Maki, *ibid.*, **39**, 1635 (1963).

(17) J. Colpa and E. de Boer, *Mol. Phys.*, **7**, 333 (1963).

(18) D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **41**, 1062 (1964).

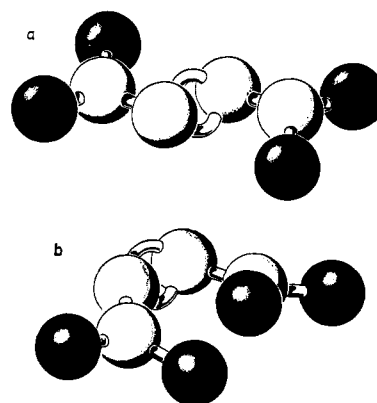


Figure 4. Possible structures for the cation of tetramethyl-2-tetrazene: (a) planar, *trans* configuration; (b) nonplanar, *cis* configuration.

The ratio, R , of the methyl proton coupling constant to the nitrogen coupling constant has previously been considered by Kuwata and Geske.¹⁰ The values of R for applicable radicals are given in Table II. The values of R for TMT^+ are consistent with those of Wurster's blue cation and with $\text{N,N}'$ -tetramethylbenzidine cation. These latter two radicals show little steric hindrance and may be contrasted with the cation of tetrakis(dimethylamino)ethylene, TDE^+ , which is very hindered. It was suggested by Kuwata and Geske that, for TDE^+ , the low values of R were due to large nonbonded electronic interactions. The values of R for TMT^+ are of comparable magnitude with the other radicals which are not sterically hindered in Table II, indicating a small amount of nonbonded interaction for TMT^+ .

Table II. Values of the Ratio, R , of the Methyl Proton Coupling Constant to the Nitrogen Coupling Constant for Related Species

Molecule	R	Ref
Wurster's blue cation	0.97	9
Tetrakis(dimethylamino)ethylene cation (TDE^+)	0.68	10
Trimethylamine cation	0.59	
$\text{N,N}'$ -Tetramethylbenzidine cation	1.48	11
Tetramethyl-2-tetrazene cation (TMT^+)	0.96	12
	1.07	This work

The TMT^+ species observed is either in the *cis* or *trans* configuration, but not both, since the spectrum is readily interpreted in terms of a single species. The *cis* configuration would lead to large nonbonded interactions (Figure 4b) similar to those observed for TDE^+ . The *trans* configuration (Figure 4a) is less hindered. The fact that R is close to the values observed for other nonhindered radical cations indicates that TMT^+ is quite likely in the *trans* rather than the *cis* configuration.

Acknowledgments. We wish to thank the Office of Naval Research for supporting this research in part, and the computer center at the U. S. Naval Postgraduate School which made the calculations possible. We wish, also, to thank Dr. Richard Knipe for helpful discussions.